Letter

Synthesis, crystal structure and magnetic properties of a novel one-dimensional heterobimetallic polymer [{Co(dpa)(DMF)(μ-SCN)$_3$Ag}$_n$] [dpa = bis(2-pyridyl)amine]

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The synthesis and X-ray characterization of a novel one-dimensional polymeric chain of cobalt(II) and silver(I) heteronuclear complexes with three different bridging thiocyanate groups are reported. The two-dimensional network is formed through hydrogen-bonding interactions of N(3)—H(1) · · · S(3) between different chains.

Crystal engineering and the design of solid-state architectures have attracted considerable attention over recent years.[1–3] Much study has been centered upon the use of supramolecular contacts and in particular hydrogen bonding between suitable organic molecules to generate multi-dimensional arrays and networks. Inorganic supramolecular chemistry has been less well developed.[4,5] Different network topologies have been developed through ligand design and the use of different transition-metal coordination numbers; this has resulted in a wide variety of structural motifs, and major advances have been made in both their theoretical descriptions and their application as new materials.[1–8] Silver(I) complexes with some soft ligands or 4,4′-bipyridyl ligands give rise to interesting polymer arrays.[5–6,8]

The properties of magneto-structural complexes with pseudohalide bridges are also of great interest.[9] However, there are few reports on cobalt(II) and other divalent first-row transition-metal complexes with bridging thiocyanate groups. Owing to the two different donor groups (N and S) within it, the thiocyanate has less versatility and is less efficient as a transmitter of magnetic interactions than the azide. It is also well-known that silver(I) ions are classified as extremely soft acids favouring coordination to soft bases, such as S and unsaturated N-containing ligands.

In this work, we report the synthesis and structural characterization of a new kind of heterometallic (Co^{II} and Ag^{I}) polymeric network with thiocyanate bridges *via* self-assembly arising most likely from the efficiency of metal-directed reactions.

The starting material in our preparation is the tricobalt complex, [Co$_3$(dpa)$_4$Cl$_2$] [dpa = bis(2-pyridyl)amido], the structure of which shows fully Co—Co bonding.[10] To a CH$_3$OH–CH$_3$CN (1 : 1) solution of [Co$_3$(dpa)$_4$Cl$_2$], AgCF$_3$SO$_3$ and an excess of NH$_4$SCN in methanol were added. A solid was obtained and then dissolved in DMF. Red crystals of heterometallic polymeric complex [{Co(dpa)(DMF)(SCN)$_3$Ag}$_n$] were formed after evaporation of the DMF solution.† X-Ray crystallography unequivocally confirmed the one-dimensional infinite-chain structure.‡

The observed electronic spectrum, measured in DMF solution, exhibits absorption maxima at λ/nm (ε/M cm^{-1}) 268(1.2 × 10^5), 315(9.3 × 10^4), 323(sh, 8.4 × 10^4) and a very weak peak at *ca.* 630 nm. The solid-state powder spectrum shows a much sharper absorption band at *ca.* 630 nm, which may be assigned to be d–d transition. This suggests that the polymer structure may be retained in solution.

The IR spectrum of the complex shows three strong absorption bands at 2120, 2112 and 2095 cm^{-1}. According to Curtis, they are assigned to the stretching vibration of C≡N of the three thiocyanate ligands.[11] The N—H stretching vibration in the dpa ligand is at 3300 cm^{-1}. A strong single peak at 1658 cm^{-1} is assigned to the CO stretching vibration in the coordi-

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† *Experimental:* A solution of AgCF$_3$SO$_3$ (154 mg, 0.60 mmol) was added to 40 ml CH$_3$OH–CH$_3$CN (1 : 1) solution of [Co$_3$(dpa)$_4$Cl$_2$] (93 mg, 0.10 mmol). An excess of NH$_4$SCN in methanol was then dropped into the mixture at room temperature. A solid was obtained and dissolved in DMF at 90 °C. The DMF solution was evaporated at room temperature, and red crystals of the heterometallic polymeric complex [{Co(dpa)(DMF)(SCN)$_3$Ag}$_n$] **1** were formed. Calcd for C$_{16}$H$_{16}$AgCoN$_7$OS$_3$: C, 32.83; H, 2.76; N, 16.75; found: C, 32.67; H, 2.87; N, 16.56%. IR (KBr pellet, /cm^{-1}): 3300, 2120, 2112, 2095, 1658, 1628, 1585, 1473, 1434, 1359, 1233, 1159, 1009, 770, 682, 527, 458 and 422.

‡ *Crystal data for* **1**. C$_{16}$H$_{16}$AgCoN$_7$OS$_3$, $M = 585.34$, triclinic, space group $P\bar{1}$; 0.52 × 0.36 × 0.20 mm^3; $a = 8.0471(1)$, $b = 11.0249(1)$, $c = 13.2676(2)$ Å, $\alpha = 72.853(1)$, $\beta = 76.486(1)$, $\gamma = 78.713(1)$°, $U = 1083.38(2)$ Å^3, $Z = 2$, $D_c = 1.794$ g cm^{-3}, λ(Mo-Kα) = 0.71073 Å. μ(Mo-Kα) = 19.81 cm^{-1}. The intensity data were collected at 293(2) K on a Siemens SMART CCD diffractometer with a detector distance of 4 cm and frame exposure time of 30 s. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL software, with 4780 unique absorption corrected (empirical, $T_{min} = 0.466$, $T_{max} = 0.741$) reflections. All non-hydrogen atoms were anisotropically refined. The refinement converged at $R = 0.0304$ and $wR = 0.0764$ for a total of 326 parameters and 4264 observed reflections with [$I > 2.0\sigma(I)$]. Atomic coordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC) reference number 440/044. See information for Authors, Issue No. 1.

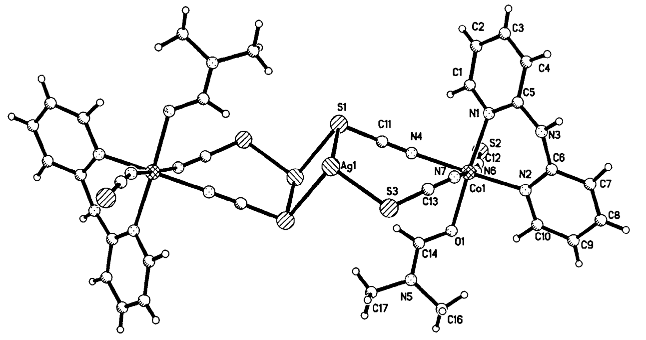

Fig. 1 ORTEP view of the complex 1. Selected bond distances (Å) and angles (°): Ag(1)—S(1) 2.6805(7), Ag(1)—S(1)^b 2.7153(7), Ag(1)—S(2)^b 2.5164(9), Ag(1)—S(3) 2.5285(8), Co(1)—N(2) 2.106(2), Co(1)—N(4) 2.108(2), Co(1)—N(6) 2.111(2), Co(1)—O(1) 2.115(2), Co(1)—N(1) 2.130(2), Co(1)—N(7) 2.205(2); S(2)^a—Ag(1)—S(3) 123.35(3), S(2)^a—Ag(1)—S(1) 96.06(3), S(3)—Ag(1)—S(1) 122.69(2), S(2)^a—Ag(1)—S(1)^b 113.33(3), S(3)—Ag(1)—S(1)^b 105.51(2), S(1)—Ag(1)—S(1)^b 91.90(2), N(4)—Co(1)—N(7) 84.23(9), N(4)—Co(1)—N(6) 92.12(10), N(7)—Co(1)—O(1) 84.67(9), S(1)—C(11)—N(4) 179.0(2), S(3)—C(13)—N(7) 178.3(2), S(2)—C(12)—N(6) 177.1(3). Symmetry transformations used to generate equivalent atoms: (*a*) *x*, *y* + 1, *z*; (*b*) −*x*, −*y* + 1, −*z* + 1

nated DMF molecule. There are two peaks, at 770(vs) and 746(sh, m) cm^{-1}, which means the coordination modes of the sulfur atoms in the three bridging thiocyanate ligands are different. The result can be confirmed by structure analysis as described later.

The coordination tetrahedron around the Ag atom formed by the two terminal S (end to end) and μ-atoms S [S(1), end-on] in the thiocyanate groups, is distorted, the coordination angles ranging from 91.90(2) to 123.35(3)°. To our knowledge, this is the first case of a complex with the coordination mode of μ-S [end-on, S(1)] in a bridging thiocyanate ligand. The average Ag—S (μ-S atom, end-on) bond length of 2.6979(7) Å is much longer than that in other two-bridging thiocyanate ligands with end-to-end S atoms [2.5164(9) and 2.5285(8) Å] and is also longer than the value in polymeric silver chalcogenides (2.564 Å).[12]

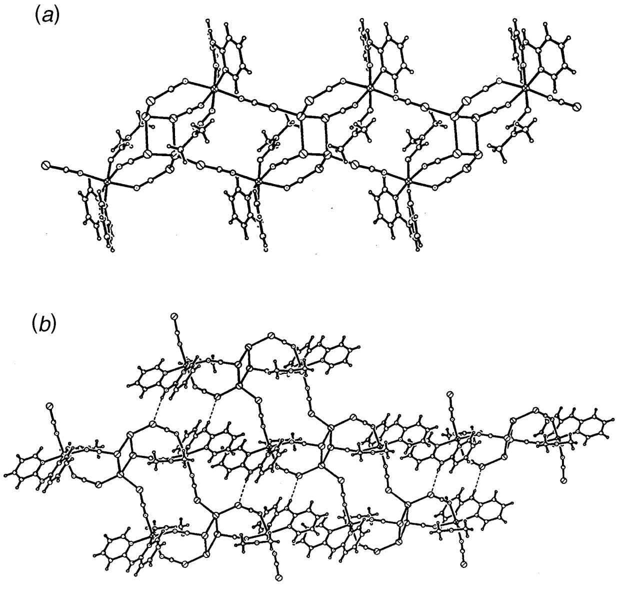

Fig. 2 (*a*) View of the three kinds of thiocyanate ligand bridged polymeric chain; (*b*) view of the packing diagram of the polymeric complex showing the two-dimensional array formed by N(3)—H(1)···S(3) hydrogen-bonding interactions

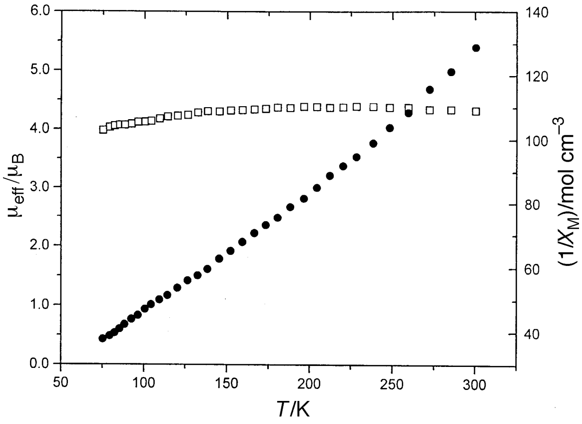

Fig. 3 Magnetic data for the [{Co(dpa)(DMF)(μ-SCN)$_3$Ag}$_n$] powder sample at 75–300 K (observed μ_{eff}, □ and χ_m^{-1} ●)

Each cobalt(II) atom is nearly octahedrally coordinated in which the two N atoms of dpa, the O atom in the bridging of DMF, and the N atom of the bridging thiocyanate group with the μ_2-S atom define an equatorial plane around the cobalt. The other two bridging thiocyanate ligands coordinate in *trans* axial positions to this plane. The lengthening of the Co—N(7) axial distance [2.205(2) Å] is related to a distortion towards an octahedron geometry around the cobalt(II) atom. The average Co—N bond length involving bridging thiocyanate groups [2.141(2) Å] is much longer than those in non-bridging thiocyanates [2.032(3) and 2.055(2) Å].[13]

The most interesting features of the structure are the three different thiocyanate ligands present in the compound and the formation of the two edge-shared Ag tetrahedra, which give rise to the one-dimensional polymeric chain of cobalt(II) and silver(I) heteronuclear complexes along the ***b*** direction. The interchain Ag···Ag contact distance in the edge-shared tetrahedra is 3.7517 Å, which is slightly longer than the weak interactions of 3.641(2) Å in [{AgL(MeCN)$_2$}BF$_4$]$_\infty$ (L = 2,7-diazapyrene).[6] The intramolecular Ag(1)···Co(1) distance is 5.398(1) Å. In the crystal, the two-dimensional network is formed through the significant hydrogen-bonding interactions between different polymeric chains [N(3)—H(1)···S(3), 3.447(2) Å] (Fig. 2).

The variable-temperature magnetic susceptibility study of the complex in the temperature range 75–300 K (Fig. 3) shows that the magnetic behaviour of the complex obeys the Curie–Weiss law with a Curie constant of 2.55 cm^3 K mol^{-1} and a Weiss temperature, θ, of −17.2 K. The value of μ_{eff} at room temperature (4.33μ_B) is larger than that expected for the spin-only case of Co^{II} (μ_{eff} = 3.87μ_B, S = 3/2, high spin) indicating that an orbital contribution is involved. The magnetic properties of this complex will be studied further.

Acknowledgements

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References

1 R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins and J. Liu, *Supramolecular Architecture*, ACS, 1992, ch. 19.
2 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.
3 G. R. Desiraju, *Crystal Engineering: Design of Organic Solids*, Elsevier, Amsterdam, 1989.

4 L. Fabbrizzi and A. Poggi, *Transitional Metals in Supramolecular Chemistry*, Kluwer, 1994.

5 A. Müller, H. Reuter and S. Dillinger, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2328; L. R. Macgillivary, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1994, 2755; S. B. Copp, S. Subramanian and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1992, **114**, 8719; S. Subramanian and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2127; B. F. Abrahams, S. R. Batten, H. Hamit, B. F. Hoskins and R. Robson, *ibid*, 1996, **35**, 1691; D. M. Goodgame, S. Menzer, A. M. Smith and D. J. Williams, *ibid*, 1995, **34**, 574.

6 A. J. Blake, N. R. Champness, A. Tov, D. A. Lemenovskii, W. S. Li and M. Schröder, *Chem. Commun.*, 1997, 1339.

7 M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 7287; L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *ibid*, 1995, **117**, 4562.

8 A. J. Blake, W. S. Li, V. Lippolis and M. Schröder, *Chem. Commun.*, 1997, 1943; M. Munakata, L. P. Wu, M. Yamamoto, T. Kuroda-Sowa and M. Maekawa, *J. Chem. Soc., Dalton Trans.*, 1995, 3215.

9 J. A. R. Navarro, M. A. Romero, J. M. Salas, M. Quirós and E. R. T. Tiekink, *Inorg. Chem.*, 1997, **36**, 4988. M. Montfort, J. Ribas and X. Solans, *Inorg. Chem.*, 1994, **33**, 4271.

10 E. C. Yang, M. C. Cheng, M. S. Tsai and S. M. Peng, *J. Chem. Soc., Chem. Commun.*, 1994, 2377; F. A. Cotton, L. M. Daniels and G. T. Jordan IV, *Chem. Commun.*, 1997, 421.

11 N. F. Cyrtis and Y. M. Curtis, *Aust. J. Chem.*, 1966, **19**, 1423.

12 Q. Huang, X. Wu and J. Lu, *Chem. Commun.*, 1997, 703.

13 G. D. Munno, M. Julve, F. Lloret, J. Faus and A. Caneschi, *J. Chem. Soc., Dalton Trans.*, 1994, 1175.

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